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Side-Chain Polyacrylates with 4-Dimethylamino-4'-stilbenecarboxylic Ester Mesogens

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Side-Chain Polyacrylates with 4-Dimethylamino-4'-stilbenecarboxylic Ester Mesogens

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ABSTRACT: ω-Acryloxyalkyl 4-dimethylamino-*trans*-stilbene-4'-carboxylates with $(CH_2)_n$ spacer chains having n = 2, 4, 6, 8, and 10 have been synthesized and polymerized to give side chain liquid crystal polymers. DSC and polarizing microscopy show that the polymers have glass and isotropization transition temperatures that decrease with increasing length of the spacer chain to T_g = 83 °C and T_i = 125 °C for the $(CH_2)_{10}$ polymer. Low isotropization enthalpies of $\leq$ 1.2 cal/g and polarizing microscopic textures indicate a low degree of order in the liquid crystal phases. The polymers are soluble, which indicates no significant cross-linking through the stilbene double bond, and the *trans* configuration of the stilbene was maintained throughout the syntheses.

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Introduction

The incorporation of mesogenic structures into flexible side chains of flexible main chain polymers often produces polymers with liquid crystalline phases, in some cases even when the analogous low molar mass compound does not exhibit a liquid crystalline phase.[1-5] The resulting side chain liquid crystalline polymers (SCLCPs) have mesophases at ambient or moderately higher temperatures, and harden to glasses with retention of liquid crystalline order when cooled from the liquid crystalline phase. Polyacrylates, polymethacrylates, and poly(methylsiloxane)s usually serve as the flexible main chains, the flexible side chains are usually polymethylene with 2 to 12 carbon atoms, and the mesogen is usually a rod-shaped structure attached at the end of the side chain. This structural scheme allows the synthesis of a wide variety of SCLCPs.

The phase transition temperatures of SCLCPs are influenced by the backbone, the side chain, the mesogen structure, and the polymer molecular weight. A more flexible backbone lowers the glass transition temperature. A longer and more flexible side chain lowers the transition temperature into a liquid crystalline phase, increases the probability of side chain crystallization at temperatures above the glass transition, and increases the probability of appearance of smectic phases. Transition temperatures increase with polymer molecular weight, and the shorter the spacer chain, the greater the dependence on molecular weight.[6,7] Traces of residual monomer depress the transition temperatures.[8]

SCLCPs with polarizable aromatic mesogens are attractive candidates for thin film second order nonlinear optical (NLO) materials.[9-13] A commonly studied second order NLO property is second harmonic generation (SHG), the doubling of the frequency of a laser beam. Second order NLO polarizability requires a non-centrosymmetric structure, and the strength of the SHG effect is enhanced by a chromophore with a large transition moment.[14] Most single crystals of achiral polar organic compounds have centrosymmetric structures, and there is no way to predict which ones will not. Consequently polymer films

for SHG investigations have been prepared using compounds with large transition moments dissolved in glassy polymers, the solute dipoles have been aligned with a strong DC electric field at temperatures near or above T_g, and the aligned materials have been hardened into the glassy state with the field still on. Three types of glassy polymer films have been prepared for second order NLO studies: (1) Polar aromatic dyes such as 4-dimethylamino-4'-nitrostilbene (DANS) dissolved in poly(methyl methacrylate) and in bisphenol-A polycarbonate and oriented in a DC field near T_g give strong SHG but lack temporal stability in the glassy state at room temperature.[15-18] Dyes dissolved in SSLCPs are more orientationally stable than in PMMA or polycarbonate.[16,19] Incorporation of the dyes into a highly cross-linked epoxy network retards but does not prevent entirely decay of the SHG with time.[20] (2) Polar aromatic compounds such as N-(4-nitrophenyl)-L-prolinol and a 4-dialkylamino-4'-nitroazobenzene derivative have been covalently bound to functional polystyrenes, poled at high temperature, and hardened to ordered glasses at room temperature.[21,22] Such compounds are not inherently liquid crystal forming, and if the poled sample relaxes in the glassy state, the molecular orientation will become more nearly isotropic. (3) SCLCPs containing mesogens with large transition moments have thermodynamically stable anisotropic glassy states.[23-35] When formed in a DC field, that state is non-centrosymmetric. Side chain LC copolymers, in which one kind of side chain contains a dye, are dichroic and have higher order parameters than dyes dissolved in SCLCPs.[23, 24]

On the premise that inherently liquid crystalline polymers will attain and retain a high degree of non-centrosymmetric order, we have prepared a series of side chain polyacrylates with polarized 4-dimethylamino-4'-stilbenecarboxylic ester mesogens which have the donor substituent at the end of the side chain and the acceptor in the spacer chain. Both the acrylate monomers (**M-n**) and the polymers (**P-n**) have LC phases at temperatures of 80 °C or higher. Other polymers that are known to form efficient SHG

films, have the donor substituent in the spacer chain and the acceptor at the end of the side chain.[26-37]

Experimental Section

Materials. 4-(N,N-Dimethylamino)benzaldehyde was recrystallized from ether. Acryloyl chloride and triethylamine were distilled under argon. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Tetrahydrofuran (THF) and 1,4-dioxane were refluxed over sodium and distilled under nitrogen. All of the other reagents and solvents were used as received.

Analytical Methods. NMR spectra were recorded on a Varian XL-300 instrument at 300 MHz for ^{1}H or 75.43 MHz for ^{13}C. All spectra were recorded in CDCl$_3$ solution with TMS as internal standard unless otherwise specified. IR spectra were taken on a Perkin Elmer 681 instrument with KBr disks. UV-visible spectra were taken on a Varian DMS 200 instrument. Elemental analyses were done at Desert Analytics (Tucson, Arizona). TLC was performed with silica gel GF thin layer chromatography plates (Analtech Inc.) with mixtures of petroleum ether and ethyl acetate as solvents. High pressure liquid chromatographic (HPLC) analyses were performed with a Waters 590 pump equipped with a normal phase 5 μm silica column (length x ID = 250 mm x 4.6 mm, Whatman PARTISIL 5), a Rheodyne injector with a 20 μL sample loop, a Beckman 153 analytical 254 nm UV detector, and an Interactive Microware data station. The eluant was 9/1 (v/v) hexane/ethanol. Molecular weights were determined by gel permeation chromatography (GPC) with the same instrument using two PL gel columns of 10^3 Å and 10^4 Å (particle size 10 μm, length x ID = 300 mm x 7.5 mm, Polymer Lab. Ltd.). THF was used as solvent (1 mL/min, 25 °C), and polystyrenes of M_n = 0.8-233 $\times 10^3$ were used as the standards for calibration. The thermal transitions were determined with a Perkin-Elmer DSC-2C differential scanning calorimeter equipped with a TADS 3600 data

station. Heating and cooling rates were 20 °C/min, unless noted otherwise. The thermal transitions were read at the maxima of the endothermic and exothermic peaks. After the first heating and cooling scans, the polymer sample was annealed at about 10 °C below the isotropization temperature for about 30 min, cooled to 25 °C at 20 °C/min, and scanned for the reported data. Glass transition temperatures (T_g) were read at the midpoint of the change in the heat capacity. The temperatures and heats of transitions were calibrated with indium as the standard. The thermal transitions and anisotropic textures were observed with a Nikon 104 optical polarizing microscope fitted with a Nikon N-2000 35 mm automatic camera and an Instec hot stage (Instec, Inc., Boulder, Colorado) that was controlled by an Apple IIe computer.

Methyl 4-(chloromethyl)benzoate (MCB). Method A. Thionyl chloride (83.3 g, 700 mmol) was added dropwise to methyl 4-(hydroxymethyl)benzoate (83.1 g, 500 mmol) cooled in an ice-water bath. The reaction mixture was heated slowly and refluxed for 10 h. The solution was poured into 500 mL of cold water and stirred, and the mixture was extracted with two 150 mL portions of ether. The combined ether extracts were washed twice with 150 mL of saturated aqueous sodium bicarbonate and once with 150 mL of water. The washed extracts were dried over 25 g of anhydrous sodium sulfate and concentrated with a rotary evaporator. The residue was distilled (bp 109 °C at 10 mmHg). After recrystallization from hexane, 74.1 g (80%) of colorless needle crystals was obtained: mp 38-39 °C (lit.[38], mp 39-40 °C).

Method B. 4-Chloromethylbenzoic acid (80.0 g, 580 mmol) and concentrated sulfuric acid (64 mL) were dissolved in 900 mL of methanol. The solution was refluxed for 1.5 h under an argon atmosphere. The reaction mixture was poured into 1 L of water, stirred, and extracted twice with 350 mL of benzene. The organic layer was washed with water and with two 350 mL portions of saturated sodium bicarbonate, and dried over sodium sulfate. The organic solution was evaporated to an oil, which was distilled (bp 109 °C at 10 mmHg) to give 83.0 g (96%) of colorless needle crystals: mp 38-39 °C.

Diethyl *p*-(Carbomethoxy)benzylphosphonate. Methyl 4-(chloromethyl)benzoate (36.9 g, 200 mmol) and triethyl phosphite (36.6 g, 220 mmol) were stirred and refluxed for 1 h under argon. Elimination of ethyl chloride started at about 130 °C, and the reaction proceeded the solution temperature rose to 187 °C. At reduced pressure, the excess triethyl phosphite was distilled out, and 52.5 g (92%) of colorless viscous liquid was obtained at 185 °C and 5 mmHg. ^{1}H NMR: δ 1.26 (t, 6 H, OCH_2CH_3), 3.24 (d, 2 H, PCH_2Ph), 3.90 (s, 3 H, CH_3O), 4.04 (m, 4 H, OCH_2CH_3), 7.4, 8.0 (m, 4 H, aromatic). ^{13}C NMR: δ 16.4 (OCH_2CH_3), 33.9 ($PhCH_2P$), 52.0 (CH_3O_2C-), 62.2 (OCH_2CH_3), 128.8, 129.8, 137.3 (aromatic), 166.8 (CH_3O_2C).

4-Dimethylamino-4'-carbomethoxy-*trans*-stilbene (*trans*-CMS). In the dark in an argon atmosphere a solution of 4-(N,N-dimethylamino)benzaldehyde (3.0 g, 20 mmol) and diethyl *p*-(carbomethoxy)benzylphosphonate (5.7 g, 20 mmol) in 30 mL of THF was added dropwise to a stirred slurry of sodium hydride (0.70 g, 30 mmol) in 60 mL of THF containing 15-crown-5 ether (30 mg) at 0 °C. Hydrogen evolved rapidly, and a yellow precipitate formed. The suspension was stirred for 2 h at 25 °C and poured into 400 mL of ice water. The precipitate was filtered and washed with ether. After recrystallization from N,N-dimethylformamide (DMF), 4.4 g (78%) of luminescent yellow crystals was obtained: mp 220-222 °C (lit.[39], mp 217-218 °C). DSC data are in Table I. ^{1}H NMR: δ 3.00 (s, 6 H, NCH_3), 3.91 (s, 3 H, OCH_3), 6.71 (d, 2 H, *ortho* to N), 6.92 (d, 1 H, J = 16.4 Hz), 7.16 (d, 1 H, J = 16.2 Hz), 7.43 (d, 2 H, *meta* to N), 7.51 (d, 2 H, *meta* to C=O), 7.99 (d, 2 H, *ortho* to C=O). ^{13}C NMR: δ 40.4 (NCH_3), 52.0 (OCH_3), 112.3 (*ortho* to N), 123.0, 125.0, 126.0, 127.8, 128.0, 130.0, 131.4, 142.8 (*para* to C=O), 150.5 (aromatic CN), 167.0 (C=O). IR: 1710 (C=O), 960 cm^{-1} (C-H). UV-vis: in $CHCl_3$ λ_{max} = 384 nm (ε = 35,700); in hexane λ_{max} = 372 nm; in methanol λ_{max} = 380 nm. Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C,76.96; H, 6.82; N, 4.92.

4-Dimethylamino-4'-carbomethoxy-*cis*-stilbene (*cis*-CMS). The cis isomer was prepared by photoisomerization of the trans isomer. *trans*-CMS (0.30 g) was dissolved in 50 mL of chloroform and exposed to normal room fluorescent lights for two days. Two spots were detected by TLC using 7% ethyl acetate and 93% petroleum ether as the solvent (*cis*-CMS, R_f = 0.27; *trans*-CMS, R_f = 0.20). The ^{1}H NMR spectrum showed that the solution was composed of 74% *cis*-CMS and 26% *trans*-CMS. The solution was chromatographed over silica gel (2.5 x 50 cm, Grade 62, 60-200 mesh, EM Science), and the *cis*-CMS was eluted with 7/93 (v/v) ethyl acetate/petroleum ether. After evaporation and crystallization from benzene 0.10 g of crystals was obtained, which contained 94% *cis*-CMS and 6% *trans*-CMS as determined from the ^{1}H NMR spectrum. ^{1}H NMR: δ 2.93 (s, 3 H, NCH_3), 6.39 (d, 1 H, J = 12.1 Hz), 6.55 (d, 2 H, *ortho* to N), 6.58 (d, 1 H, J = 11.9 Hz), 7.43 (d, 2 H, *meta* to N), 7.51 (d, 2 H, *meta* to C=O), 7.99 (d, 2 H, *ortho* to C=O). ^{13}C NMR δ 40.3 (NCH_3), 52.0 (OCH_3), 111.7 (*ortho* to N), 124.4, 125.6, 128.0, 128.0, 128.7, 129.5, 130.0, 132.3, 143.3 (aromatic *para* to C=O), 149.8 (NC), 167.1 (C=O). IR: 1720 (C=O), 715 cm^{-1} (C-H). UV-vis (CHCl$_3$): λ_{max} = 375 nm (ε = 13,700).

ω-Hydroxyalkyl 4-dimethylamino-*trans*-stilbene-4'-carboxylates (A-n). All alcohols A-n were synthesized by the transesterification of *trans*-CMS with excess diol in the presence of concentrated sulfuric acid. A typical procedure is illustrated with the synthesis of A-8. *trans*-CMS (11.2 g, 40 mmol), 1,8-octanediol (200 g, 1.37 mol), and concentrated sulfuric acid (3.5 mL) were stirred at 90 °C for 36 h under argon in the dark. The reaction was monitored by TLC using 1/1 ethyl acetate/petroleum ether as the solvent. The solution was poured into 2 L of water and stirred. The yellow precipitate was filtered and recrystallized from methanol to yield 9.8 g (62%) of yellow product with a purity of 99% (HPLC). IR: 3520-3440 cm^{-1} (OH). The ^{1}H NMR and ^{13}C NMR spectra were nearly identical with those of *trans*-CMS with the expected addition signals from

the C_8 chain. UV-vis (**A-10**, CHCl$_3$): λ_{max} = 384 nm (ϵ = 45,900). Yields and thermal

analyses are reported in Table II. **A-8** and **A-10** had C, H, and N analyses within 0.2%

of the calculated values. The other **A-n** compounds were not analyzed.

ω-Acryloxyalkyl 4-dimethylamino-*trans*-stilbene-4'-carboxylates

(**M-n**). The acrylate monomers were synthesized by the esterification of the

corresponding alcohols (**A-n**) with acryloyl chloride. For example, **M-8** was prepared as

follows. Under argon in the dark **A-8** (9.20 g, 23 mmol), triethylamine (5.10 g, 50

mmol) and 300 mL of THF were stirred at 0 °C. Acryloyl chloride (4.80 g, 50 mmol) was

added dropwise. The mixture was allowed to warm to 25 °C and stirred for 12 h. The

reaction was monitored by TLC with 1/1 ethyl acetate/petroleum ether as the solvent. The

yellow suspension was poured into 2 L of water and stirred. The precipitate was filtered

and recrystallized from methanol to give 9.0 g (86%) of yellow crystals with a purity

higher than 99.0% (HPLC). IR: 1715 cm^{-1} (C=O); there was no O-H stretching band.

The ^{1}H NMR and ^{13}C NMR spectra were nearly identical with those of *trans*-CMS and

the **A-n** compounds except for the expected ^{1}H acrylate signals (for **M-8**) at δ 5.81 (d, J =

10.2 Hz), 6.12 (dd, J = 17.4, 10.5 Hz), and 6.40 (d, J = 10.5 Hz), and ^{13}C acrylate

signals (for **M-8**) at δ 128.2, 130.5, and 166.4 (C=O). UV-vis (**M-10**, CHCl$_3$): λ_{max} =

384 nm (ϵ = 38,400). Yields and DSC data are reported in Table II. **M-8** and **M-10** had

C, H, and N analyses within 0.2% of the calculated values. The other **M-n** compounds

were not analyzed.

Acrylate Polymers (P-n). Method A (for **P-2**, **P-4**, **P-6**, **P-8**, and **P-10**).

The acrylate monomers (**M-n**), each 0.50 g, were polymerized as 10% (w/v) solutions in

1,4-dioxane with 1.0 wt % AIBN as initiator. The solution in a glass tube was degassed

by three freeze-pump-thaw cycles under vacuum, sealed, and held in a water bath at 60 °C

for 60 h. The solution was poured into methanol to precipitate the polymer. The polymer

was filtered, dried under vacuum, and reprecipitated from THF into methanol. The yields

and DSC and GPC characterizations of the polymers are reported in Table II.

Method B (for **P-8B** and **P-10B**). The monomers **M-8** (8.40 g) and **M-10** (12.50 g) were separately dissolved with 1 wt % of AIBN into 76 mL and 104 mL of 1,4-dioxane in 200 mL flasks equipped with condensers. The solutions were purged with argon for 2 h, heated at 65 °C for 96 h, and poured into methanol to precipitate the polymers. The polymers were filtered and dried under vacuum to yield 5.47 g (65%) and 7.8 g (62%) of crude products. After reprecipitation from THF into methanol, 2.63 g (31%) of **P-8B** and 5.11 g (41%) of **P-10B** were obtained. GPC and DSC characterizations are reported in Table II. ^{1}H NMR (**P-10**, $CDCl_2CDCl_2$, 90 °C): The narrowest lines were 8 Hz wide at half-height. Otherwise the spectrum was like that of **M-10**, including doublets at δ 6.93 and 7.15 (J = 16 Hz), lacking the vinyl H signals, and with additional broad bands at δ 1.3 and 1.7 (backbone CH_2) and 2.9 (backbone CH). ^{13}C NMR ($CDCl_2CDCl_2$, 90 °C): The spectrum of **P-10** was nearly identical with that of **M-10**. The signal-to-noise ratio was too low to detect peaks from backbone or acrylic ester carbonyl carbons. UV-vis (**P-10**, $CHCl_3$): λ_{max} = 384 nm (ε = 20,200). Anal. of **P-8B**. Calcd for $C_{28}H_{35}NO_4$: C, 74.80; H, 7.85; N, 3.12. Found: C, 74.54; H, 7.93; N, 3.24. Anal. of **P-10B**. Calcd for $C_{30}H_{39}NO_4$: C, 75.44; H, 8.23; N, 2.93. Found: C, 75.45; H, 7.97; N, 2.99. The polymers made by method A were not analyzed.

Results

The monomers and polymers were synthesized as shown in Scheme I. The key double bond forming step was performed by a Wadsworth-Emmons reaction using 15-crown-5 ether as a catalyst to provide 78% yield of 4-dimethylamino-4'-carbomethoxy-*trans*-stilbene (*trans*-CMS) from the rather unreactive *p*-dimethylaminobenzaldehyde. *trans*-CMS was prepared before in low yield via hydrolysis of 4-dimethylamino-4'-cyanostilbene.[39] The ^{1}H NMR spectra of *trans*-CMS and all of the alcohols **A-n** and acrylate monomers **M-n** showed only the *trans*-stilbene isomer. *trans*-CMS, the alcohol **A-10**, the monomer **M-10**, and the polymer **P-10** all have a bright yellow color and identical absorption maxima at 384 nm in $CHCl_3$. Thus the entire synthesis proceeded without detectable isomerization of the stilbene double bond.

In an early experiment the color of an NMR sample of *trans*-CMS in $CDCl_3$ turned red during a few days in flourescent lighting, and new peaks for *cis*-CMS appeared in the ^{1}H NMR spectrum. From such a photoisomerized mixture on a larger scale 94% pure *cis*-CMS was isolated chromatographically. The mixtures of *cis*-CMS and *trans*-CMS are analyzed easily by the relative areas of the NCH_3 signals in their ^{1}H NMR spectra. *cis*-CMS is yellow too, but not as intensely colored as *trans*-CMS.

The phase transition temperatures of alcohols **A-n** and acrylate monomers **M-n** determined by DSC are reported in Table I. Only a melting transition was observed for each of the alcohols. The acrylates all had a melting transition with a large ΔH_m and a mesophase to isotropic transition with $\Delta H_i < 0.6$ kcal/mole of repeat units. Typical DSC thermograms of the C_{10} compounds are shown in Figure 1. The transition temperatures decrease systematically, and the temperature range of the liquid crystalline phase increases, with increasing length of the polymethylene chain as shown in Figure 2. Polarizing microscopic examination of each compound showed transitions at about the same

temperatures observed by DSC. A typical texture of the liquid crystalline phase of M-10 is shown in Figure 3.

The monomers M-n were polymerized with 1% AIBN initiator in dioxane solutions. GPC analyses of the molecular weights based on polystyrene standards and DSC analyses of the phase transitions of the polymers P-n are reported in Table II. All polymers were precipitated from the reaction mixtures and reprecipitated once from THF into methanol. The samples prepared from 0.5 g of monomer had M_n = 2,800-5,700, whereas P-8B and P-10B, prepared from about 10 g of monomer, had M_n = 11,000. The higher molecular weight samples had higher glass and isotropic transition temperatures. The T_g and T_i decreased systematically, and the temperature range of the liquid crystalline phase increased with increasing length of the polymethylene spacer chain, as shown in Figure 4. No other transitions were found for any annealed polymer in the temperature range between 0 °C and the T_g reported in Table II. Repeated DSC scans after the first showed approximately the same phase transitions, but after many cycles and long annealing times between repeated heating scans, the peaks became smaller as shown for P-8 in Figure 5. All data reported in Table II are from the second heating scan after a 30 minute annealing period at 10 degrees below T_i during the first cooling scan.

The polarizing microscopic textures of the polymers were nondescript until the samples were annealed for 24 hours at temperatures five to ten degrees below the isotropic transition. Such treatment gave the textures of P-8B and P-10B shown in Figure 6. The shorter spacer chain polymers gave less well defined textures.

Discussion

All of the polyacrylates P-n have small ΔH_i indicative of a liquid crystal phase of low degree of order. The ΔH_i data in Table II were obtained with samples that were annealed briefly before the DSC heating scan, but only P-8B was scanned repeatedly, as

shown in Figure 5. The ΔH_i data in Figure 5 show $\Delta H_i = 0.45$ cal/g for one scan after a short annealing time, and $\Delta H_i = 0.38, 0.45$, and 0.29 cal/g for three scans after long annealing times, which suggests that the other SCLCP ΔH_i data are probably reliable to within about 0.1 cal/g of the reported values in Table II. Typically ΔH_i for polymer nematic phases are < 1.0 cal/g, whereas the least ordered smectic phases, S_A and S_C, typically have ΔH_i of >1.0 cal/g.[2,3] (There are exceptions.) The ΔH_i includes contributions from loss of order of both the spacer chains and the mesogens. Longer spacer chains give larger ΔH_i. Figure 7 shows that T_g and T_i of the polymers and T_m and T_i the monomers depend approximately on the mass fraction of the stilbene component of the structure. The small ΔH_i values of our annealed polymers indicate a low degree of order of both the mesogens and the spacer chains in the liquid crystalline states. The microscopic textures of **P-8** and **P-10** do not allow unambiguous assignments of the phases, but they are consistent with nematic or S_A phases. Although we cannot identify the polymer phases with certainty without additional experiments, such as X-ray scattering, both DSC and microscopic results are consistent with nematic phases.

The polymers have unusually high T_g's compared with other side chain polyacrylic esters,[1-5] which we attribute to the influence of the highly dipolar mesogens on the main chain mobility.

The monomers **M-n** also have low ΔH_i values of ≤ 1.3 cal/g indicative of nematic phases. **M-10** showed three phase transitions, but the other **M-n** compounds showed only two. The first transition of **M-10** at 94 °C (Figure 1) occured without change in its polarizing microscopic texture and without flow, which suggests that it may be a solid-solid transition, although we cannot rule out the possibility that the phase at 94-126 °C is some highly ordered mesophase.

When M_n is greater than 10,000 by GPC (based on polystyrene standards) the phase transition temperatures of poly{6-[4-methoxy-(4'-oxy)-α-methylstilbene]hexyl methacrylate} side chain liquid crystal polymers do not depend on molecular weight.[40]

The T_g and T_i data in Table II show that $M_n = 3,400\text{-}5,100$ (**P-8** and **P-10**) is not high enough to attain the maximum transition temperatures of high molecular weight SCLCPs. By comparison with the previous stilbene methacrylates[40] we presume that the **P-8B** and **P-10B** transition temperatures are the maximum values.

Stilbenes are known to photoisomerize and photodimerize and to react at the central double bond during certain free radical polymerizations. *trans*-Stilbene reacts readily with the benzoyloxy radical from dibenzoyl peroxide but not with the 1-cyano-1-methylethyl radical from AIBN.[41] We used AIBN to initiate polymerizations. Copolymerization of acrylate and stilbene double bonds would give cross-linked polymers. Photodimerization of stilbene double bonds, of either the monomers before polymerization or of the polymers during or after polymerization, could also give cross-linked polymers. Photoisomerization of stilbenes is much faster than photodimerization in homogeneous solutions, but dimerization may be favored in the solid state[42] and in ordered assemblies such as bilayers.[43] There was no evidence of cross-linking of any of our polymers. They all dissolved readily in THF for purification by precipitation, and also dissolved in dioxane and chloroform. After we observed photoisomerization of *trans-CMS* to *cis-CMS* in solution in fluorescent lighting, we stored all stilbene samples out of light and observed no other evidence of photoisomerization.

Our stilbene SCLCPs are designed to have second order nonlinear optical properties due to the large transition moments of the donor-acceptor substituted conjugated aromatic structures. Related stilbenes have large second order NLO polarizabilities.[44-46] The structures were chosen partly on the basis of ease of synthesis. The dimethylamino group is the strongest donor group available in commercial starting materials. Carboxylic esters are not the strongest acceptors available, but they are easily attached to the spacer chains of SCLCPs. The stilbene polyacrylates are soluble in several solvents, and thin films have been spin coated onto glass substrates in preliminary experiments. The films should be suitable for nonlinear optical studies.

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Table I

Characterization Data of *trans*-CMS, A-n, and M-n.

compound	% yield	T_m, °C	ΔH_m, kcal/mol (cal/g)	T_i, °C	ΔH_i, kcal/mol (cal/g)
trans-CMS	78	229	8.78 (31.2)		
A-2	69	216	5.14 (23.3)		
A-4	74	191	5.09 (15.0)		
A-6	69	170	5.07 (13.8)		
A-8	65	159	4.94 (12.5)		
A-10	61	149	5.00 (11.8)		
M-2	49	178	3.76 (10.3)	196	0.04 (0.1)
M-4	34	153	3.42 (8.7)	181	0.43 (1.1)
M-6	72	142	3.79 (9.0)	175	0.55 (1.3)
M-8	86	133	3.96 (8.8)	166	0.22 (0.5)
M-10	90	126	3.87 (8.1)	159	0.29 (0.6)

The column headers T_m, ΔH_m, T_i, ΔH_i appear under a spanning header -----DSC (heating)-----.

Table II

Characterization Data of Polymers

polymer	% yield[b]	GPC[a]		DSC (heating)		
		M_n x10^{-3}	M_w x 10^{-3}	T_g, °C	T_i, °C	ΔH_i, kcal/mole (cal/g)
P-2	48	5.7	14.3	129	139	0.09 (0.25)
P-4	20	2.8	7.1	119	130	0.28 (0.72)
P-6	26	3.9	9.7	109	125	0.41 (0.98)
P-8	24	3.4	9.1	91	121	0.52 (1.16)
P-8B	31	11.0	27.6	96	130	0.18 (0.41)
P-10	27	5.2	10.3	81	117	0.58 (1.21)
P-10B	41	10.9	36.9	83	125	0.43 (0.89)

[a]THF solvent; polystyrene standards. [b]After reprecipitation.

Scheme 1

ClCH₂—⟨benzene⟩—CO₂H   HOCH₂—⟨benzene⟩—CO₂CH₃

$$ClCH_2\text{—}\langle C_6H_4\rangle\text{—}CO_2H \xrightarrow[\text{H}_2\text{SO}_4]{\text{CH}_3\text{OH}}$$

$$HOCH_2\text{—}\langle C_6H_4\rangle\text{—}CO_2CH_3 \xrightarrow{\text{SOCl}_2}$$

$ClCH_2$—⟨benzene⟩—CO_2CH_3

$$\xrightarrow{\text{P(OC}_2\text{H}_5)_3}$$

$(CH_3)_2N$—⟨benzene⟩—CHO

$(C_2H_5O)_2POCH_2$—⟨benzene⟩—CO_2CH_3 $\xrightarrow{\text{NaH, 15-Crown-5, THF}}$

$(CH_3)_2N$—⟨benzene⟩—CH=CH—⟨benzene⟩—CO_2CH_3

trans-CMS $\xrightarrow[\text{H}_2\text{SO}_4]{\text{HO(CH}_2)_n\text{OH}}$

$(CH_3)_2N$—⟨benzene⟩—CH=CH—⟨benzene⟩—$CO_2(CH_2)_nOH$

A-n $\xrightarrow[\text{Et}_3\text{N, THF}]{\text{ClC(O)CH=CH}_2}$

$(CH_3)_2N$—⟨benzene⟩—CH=CH—⟨benzene⟩—$CO_2(CH_2)_nO_2CCH=CH_2$

M-n $\xrightarrow[\text{1,4-Dioxane}]{\text{AIBN}}$

$(CH_3)_2N$—⟨benzene⟩—CH=CH—⟨benzene⟩—$CO_2(CH_2)_nO_2C\text{-CH}$

P-n $n = 2, 4, 6, 8, 10$

Figure Captions

Figure 1. DSC thermograms of **A-10**, **M-10**, and **P-10** at 20 deg/min.

Figure 2. Dependence of melting and isotropic transition temperatures of monomers **M-n** on spacer chain length.

Figure 3. **M-10** between crossed polarizers (200x) after cooling slowly to 110 °C.

Figure 4. Dependence of glass and isotropic transition temperatures of polymers **P-n** on spacer chain length.

Figure 5. Repeated DSC analyses of **P-8B**. (a) first heating; $\Delta H_i = 0.45$ cal/g. (b) first cooling, after 2 min at 180 °C. (c) second heating, after 5 min at 25 °C. (d) second cooling, after 2 min at 180 °C. (e) third heating, after 26 h at 100 °C and cooling to 25 °C; $\Delta H_i = 0.38$ cal/g. (f) third cooling, after 2 min at 180 °C. (g) fourth heating, after 60 h at 100 °C and cooling to 25 °C; $\Delta H_i = 0.45$ cal/g. (h) fourth cooling, after 2 min at 180 °C. (i) fifth heating, after 100 h at 100 °C and cooling to 25 °C; $\Delta H_i = 0.29$ cal/g. (j) fifth cooling, after 2 min at 180 °C.

Figure 6. (a) **P-8B** and (b) **P-10B** between crossed polarizers (50x) after 10 h at 125 °C.

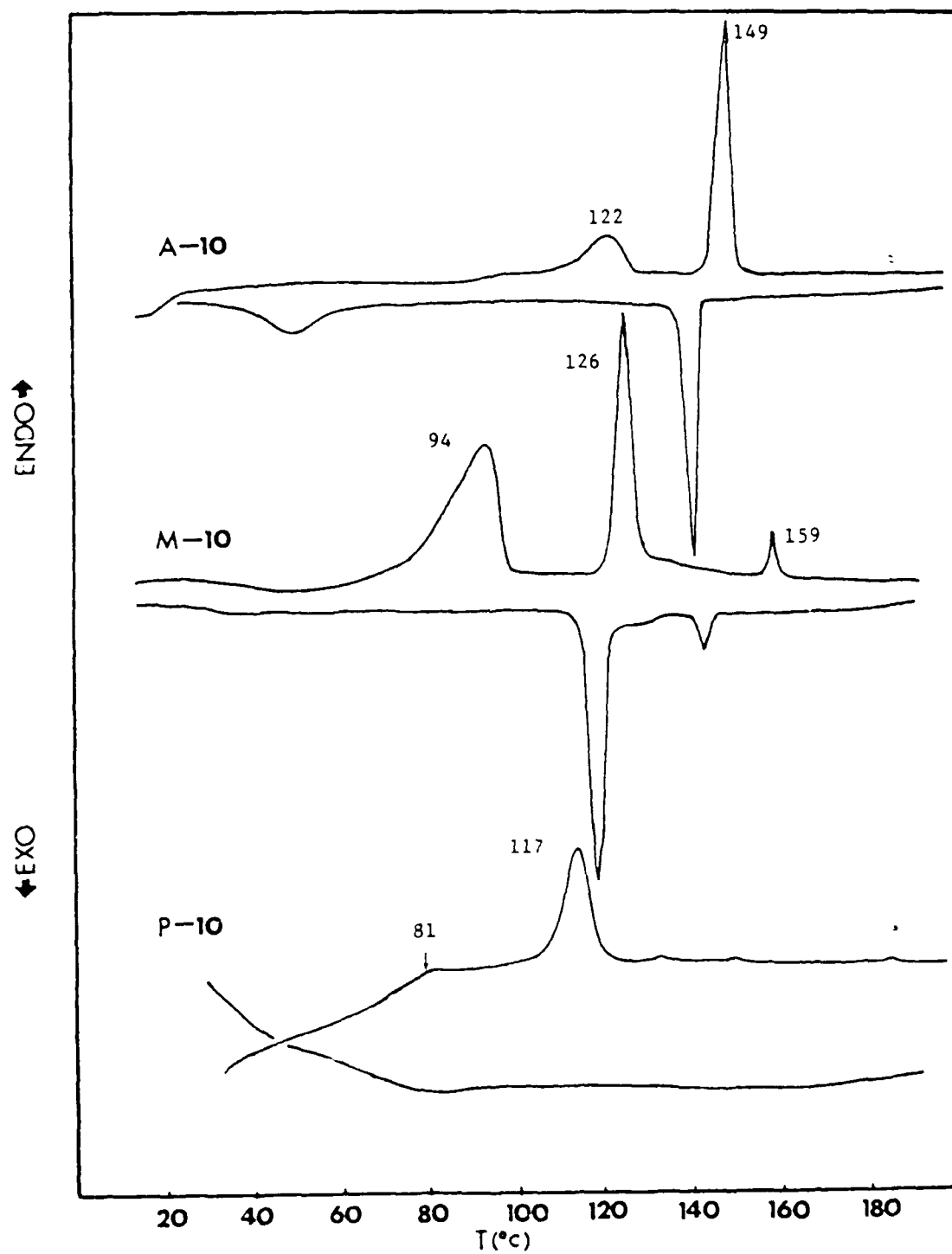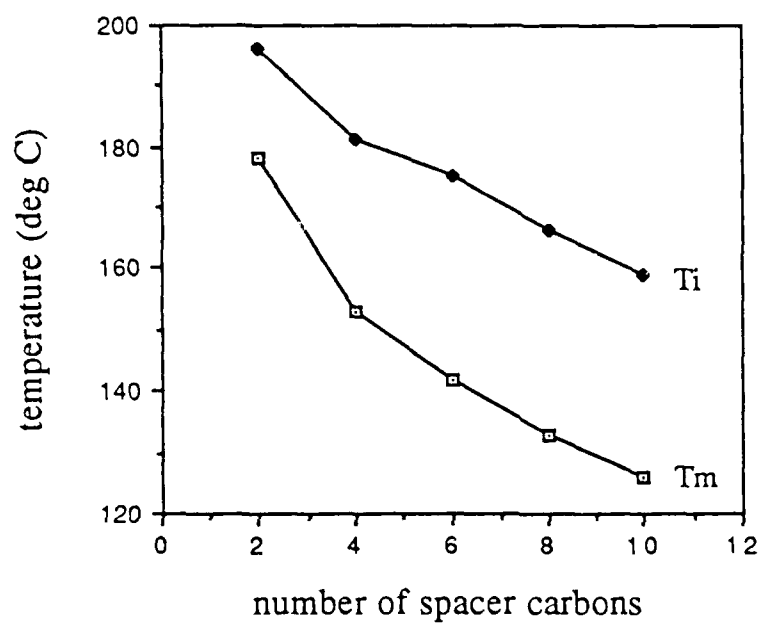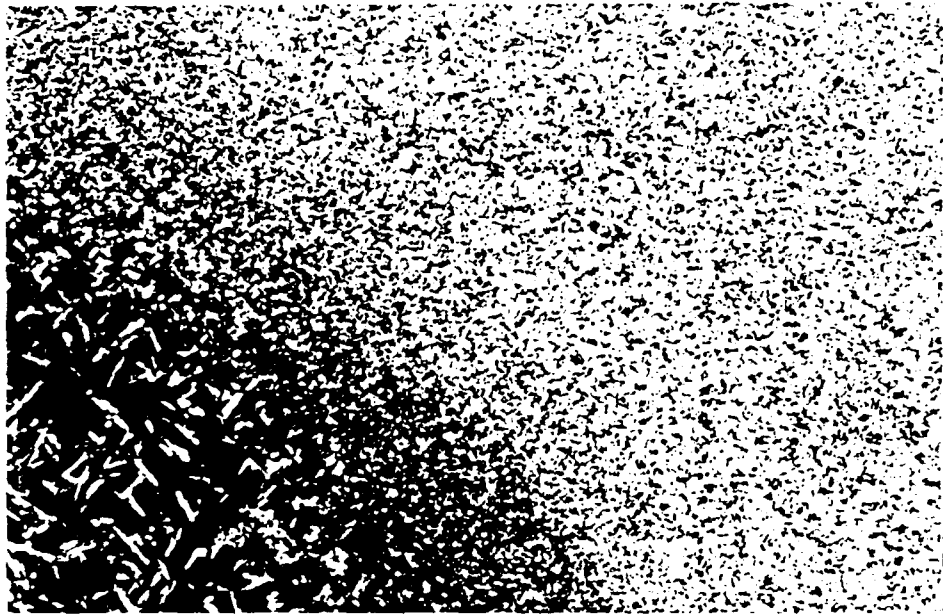**Figure 7.** Dependence of phase transition temperatures on weight % of stilbene mesogen in sample.

Figure 1
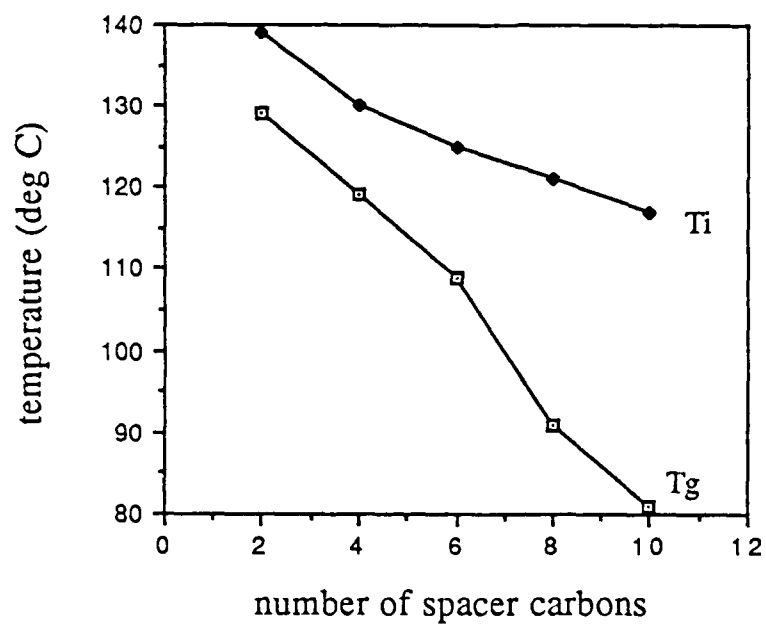
Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

a

b

Figure 7